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NOTES ON THE DEVELOPMENT OF THE RUBY COLOR IN GLASS

BY

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NOTES ON THE DEVELOPMENT OF THE RUBY COLOR IN GLASS

BY A. E. WILLIAMS

The term "ruby glass" is applied to red glass colored by the use of copper, gold, selenium and in some cases, flowers of sulphur, the color varying considerably in intensity and shade. In case of copper, the color varies from amber to various shades of reds to brown and to opaque black. With gold the red has a rose tint, and selenium ruby seems to be a brighter red of varying intensities. The red from sulphur is rather unreliable, in that a uniform color is hard to obtain, and therefore only used for lower grades of glass.

Copper and gold reds are said to be due to the metals in suspension as colloids.

V. Pöschl[1] describes the preparation of Purple of Cassius from gold, and shows that the red or the purple gold-hydrosol may be obtained, depending upon the proper electrolyte present.

Paal's[2] process for the preparation of colloidal solutions shows that a red or blue hydro-sol of copper is obtained, depending upon the properties of the solutions.

In G. Bredig's[3] method of producing colloids electrolytically, he obtained finely divided metallic gold, dark purple in color, when the arc takes place under distilled water. If a trace of caustic soda is added, deep red color is obtained.

That copper and gold are in the same condition in glass as in solutions is proven by the use of the ultra-microscope.

Zsigmondy[4] says that ruby glass will become red, or remain colorless upon slow cooling according to its quality. It will always remain colorless on chilling, the normal red color generally being brought out upon reheating to the softening point; (high lead glasses show yellow or brown instead of red). The coloring is due to the gold, which is at first homogeneously dissolved in

[1] V. Poschl, *Chemistry of Colloids,* p. 55.
[2] Ibid, p. 66.
[3] Ibid, p. 67.

the glass, later separating out in the form of ultra-microscopic particles which reflect green light.

He compares this phenomenon with devitrification, and refers to Tammann's[5] work on devitrification. Tammann shows that the speed of crystallization, and the ability to crystallize increase with diminishing temperature from the melting point and then decrease again, while viscosity steadily increases. Zsigmondy applies Tammann's results to ruby glass in this manner:

"Ruby glass is worked several hundred degrees lower than its melting temperature. At the working temperature, conceive it as a super-saturated crystalloid solution of metallic gold and the smallest amicroscopic particles to be centers of crystallization, it will at once be seen why ruby glass sometimes remains colorless upon simple cooling. In this case the optimum temperature for spontaneous crystallization is so low that the glass is very viscous and the speed of crystallization reduced to a minimum. If by reheating, the glass acquires a certain mobility, the gold separates out upon the nuclei present which by growth become sub-microns, visible in the ultra-apparatus and turning the glass red or darker."

V. Pöschl[6] says that gold ruby is obtained by an addition of gold chloride to the glass melt from which particles of gold separate out, when the mass is quickly cooled. These particles, however, have the magnitude of amicrons, so that the glass appears colorless. By heating anew until the glass becomes soft, the particles grow until they attain the size of ultra-microns, to which the cause of the red color is traced. The preparation of copper ruby glass is performed by an analogous method.

Copper ruby has, in the past, been made by a process known as flashing. This process is described somewhat as follows by Rosenhain:[7]

"Flashing glass is the process of placing a very thin layer of colored glass on the surface of a more or less colorless glass of usual thickness. This is generally accomplished by taking a small gathering of the colored glass on the pipe, and the remaining gathering for the piece to be made from the colorless glass pot. When this glass is blown, the ruby glass lies in a thin layer over the inner surface of the cylinder. The special skill required is in blowing this layer to a uniform thickness to obtain a uniform color."

[4] Zsigmondy, *Colloids and the ultra-microscope*, p. 165.
[5] Tammann, *Zeit. for Electro-chemi*, 1904, Vol. 10, p. 532.
[6] Ibid I, p. 103.
[7] Walter Rosenhain, *Glass Manufacture*.

The necessity of flashing is due to the density of the color. Copper colors are so dense that many glasses are opaque when over 3 m.m. thick, the color depending upon the composition and rate of cooling. However, it is possible to control the density of the color somewhat in the flashed ruby glass by carefully controlling the temperature of working the glass and rate of cooling in the molds.

These factors must be controlled very carefully in practice to produce uniform results. If these glasses are cooled very quickly, as for instance, chilling in water or rolling very thin (2 m.m. thick) on an iron plate, the red color will not develop, or at least shows only in scattered streaks. By reheating at definite temperatures, the color may be obtained in varying degrees of intensity from amber to opaque black, depending upon the temperature to which the glass is reheated. Thus it will be seen that the temperature and rate of cooling must be constant, to produce a uniform shade of red when this color is developed during blowing.

At the present time, however, copper ruby glass is being made in which the color does not come out in the pressing or working, but is brought out later by reheating. The density of the color in this glass is very much less than the flashed ruby glass, and pieces of greater thickness can be easily made. The color range from a light amber through reds to a dense opaque black, with an increasing temperature.

Available literature consulted on the subject gave no complete or definite methods for working ruby glass, but emphasized the necessity for care.

The following are some formulae and directions obtained:

Gerner,[8] gives a history of copper ruby glass and a number of mixes with methods of handling. The following are two of the batches given by him:

[8] Gerner, *"Glass,"* p. 195.

GERMAN COPPER GLASS

100.0	Sand
25.0	Potash
17.0	Borax
2.5	Cu_2O
5.0	SnO_2
0.2	Fe_2O_3
2.5	MnO_2
0.5	Bone ash

Calculated Formula[9]

$$\left.\begin{array}{l} 0.200\ PbO \\ 0.390\ K_2O \\ 0.120\ Na_2O \\ 0.095\ CuO \\ 0.079\ MnO \\ 0.014\ CaO \end{array}\right\} \begin{array}{l} 0.0060\ Fe_2O_3 \\ 0.2500\ B_2O_3 \\ 0.0044\ P_2O_5 \end{array} \left\{ \begin{array}{l} 4.36\ SiO_2 \\ 0.09\ SnO_2 \end{array}\right.$$

FRENCH COPPER GLASS

$$\left.\begin{array}{r} 100\ SiO_2 \\ 50\ Pb_3O_4 \\ 25\ K_2CO_3 \\ 5\ NaNO_3 \end{array}\right\}$$

This batch is fused, chilled, dried, ground and mixed with 1 Cu_2O, 1.5 SnO_2, 5 cream of tartar. This is melted and blasted one hour during melt.

Calculated Formula

$$\left.\begin{array}{l} 0.534\ PbO \\ 0.346\ K_2O \\ 0.074\ Na_2O \\ 0.046\ CuO \end{array}\right\} \begin{array}{l} 3.900\ SiO_2 \\ 0.034\ SnO_2 \end{array}$$

Notes on ruby glass from Sprechsaal[10] give the following by translation:

"In the manufacture of ruby glass it is not in the field of the furnace man to control the color. Repeated fusion and cooling makes the best color, and the color does not depend as much upon the percent of coloring oxide in the mix as upon the temperature of the glass while working, the rate of fusion and rate of cooling the finished piece." The following batch is given:

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[9] The empirical formulae of all glasses given in the following work were calculated by the writer.

[10] *Sprechsaal*, Feb. 6, 1913, p. 92.

	LIGHT RED	DARK RED
Sand	100.0 kg.	100.0 kg.
Soda ash	16.0 kg.	16.0 kg.
Potash	16.0 kg.	16.0 kg.
Borax	4.0 kg.	6.0 kg.
Whiting	10.0 kg.	12.0 kg.
Witherite	10.0 kg.	10.0 kg.
Cu_2O	2.0 kg.	4.0 kg.
SnO_2	2.0 kg.	4.0 kg.
Fe_2O_3	0.5 kg.	1.0 kg.
Cream of tartar	0.8 kg.	1.3 kg.

Calculated Molecular Formula

$$\left.\begin{array}{l} 0.385\ Na_2O \\ 0.210\ K_2O \\ 0.222\ CaO \\ 0.110\ BaO \\ 0.064\ CuO \end{array}\right\} \begin{array}{l} 0.0066\ Fe_2O_3 \\ 0.0660\ B_2O_3 \end{array} \left\} \begin{array}{l} 3.63\ SiO_2 \\ 0.03\ SnO_2 \end{array}\right.$$

"The manufacture of ruby glass demands great care and practice in working. This is especially so with pressed glass. The raw batch should be put into a preheated pot and melted six hours. The melt is blasted several times and poured into cold water for remelting and refining. If the pressed pieces are not colored enough they can be reheated. The mold must not be too hot to allow the glass to cool too slowly, or too cold to chill and cause the pieces to crack. The following batch is also given:"[11]

Sand	100.0 kg.
Potash	25.0 kg.
Red lead	25.0 kg.
Borax	10.0 kg.
Soda	5.0 kg.
Cu_2O	3.5 kg.
SnO_2	2.0 kg.
Fe_2O_3	0.5 kg.
MnO_2	0.5 kg.
Cullet	25.0 kg.
Cream of tartar	0.5 kg.

[11] Ibid 10, p. 92.

Calculated Molecular Formula

$$\left.\begin{array}{l} 0.2020\ K_2O \\ 0.6230\ PbO \\ 0.1010\ Na_2O \\ 0.0668\ CuO \\ 0.0079\ MnO_2 \end{array}\right\} \begin{array}{l} 0.00418\ Fe_2O_3 \\ 0.07250\ B_2O_3 \end{array} \left\{ \begin{array}{l} 2.310\ SiO_2 \\ 0.018\ SnO_2 \end{array}\right.$$

Rudolf Hohlbaum[12] says that red colors may be obtained by the use of Cu_2O, selenium, sulphur and gold, but is most often obtained from Cu_2O. He gives the following batch for a copper ruby:

100.0 SiO_2	
34.0 K_2CO_3	
16.0 $CaCO_3$	K_2CO_3=80 to 85 percent pure
0.6 Cu_2O	
2.0 SnO_2	

Calculated Formula

$$\left.\begin{array}{l} 0.536\ K_2O \\ 0.440\ CaO \\ 0.023\ CuO \end{array}\right\} \begin{array}{l} 4.570\ SiO_2 \\ 0.041\ SnO_2 \end{array}$$

Hohlbaum says:

"Concerning the mixing of the Cu_2O, I wish to remark that it is possible to obtain the ruby color with 0.4 percent Cu_2O, also with 0.8 percent. However, with 0.8 percent of the batch as Cu_2O the color is so dense that large masses are not workable. As such a small quantity of Cu_2O is needed to make ruby, it is mixed best by using 0.8 percent Cu_2O and SnO with half the batch of glass. When the glass is ready to blast then mix the batch containing 0.8 percent Cu_2O with an equal batch of crystal glass, and a 0.4 percent Cu_2O batch is obtained which gives a weaker color. It is best to employ SnO as a reducing agent to insure the obtaining of a ruby color, and one finds from practical experience that the mix must contain less than double the quantity of Cu_2O as SnO. If this is not sufficient reducing agent, cream of tartar may be used in quantities to satisfy all conditions. Iron scale may also be used as a reducing agent but the pure ruby color is then changed."

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[12] R. Hohlbaum, *Seitgemasse Herstellung Bearbeitung vnd Verzierung des Feinern Holglases,* p. 125.

Hohlbaum[13] gives the following batch for a gold ruby:

Rose Color

Sand	100.0 kg.
Potash	34.0 kg.
Calcium carbonate	17.0 kg.
Gold	16.0 gms.

Gold must be brought into the mix in a very finely separted form, best in solution or as Purple of Cassius.

To get the gold in solution, it must be cut into small pieces and dissolved with aqua regia. The gold solution is poured on part of the mix, and this mixed with the balance of the batch.

In the heat of the oven, the decomposition of the gold chloride takes place so rapidly, that a portion of the gold chloride is carried away undecomposed. There is, therefore, not so much gold dissolved in the glass as is introduced, and the color is much weaker than it would be, if all the gold were dissolved. It is, of course, reasonable for one to try and reduce the vaporization of the gold chloride as much as possible. This may be done by pouring the gold chloride on 1 kgm. of sand and evaporating to dryness. Then mix this well with half of the batch, or use gold purple in the same manner.

According to Hohlbaum's experience, either phosphoric acid or barium work favorably in the making of gold ruby, causing the gold to separate out more rapidly. Without either, the ruby is too light. A batch for making a rose glass with a violet tinge with the use of barium is given.

Rose Glass with Barium

Sand	100.0 kgm.
$BaCO_3$	16.0 kgm.
95 percent soda, Na_2CO_3	43.0 kgm.
Gold	12.0 gms.

Selenium Ruby, Light and Rose Colored

Arsenic	200.0 gms.
Sand	100.0 kgm.
Potash, 80-85 percent	34.0 kgm.
$CaCO_3$	17.0 kgm.
Selenium nitrate	120.0 gms.

[13] Ibid 12, p. 126.

In the reds with sulphur, one should not use the alkali sulphates, but only sulphur with charcoal as a reducing agent. The charcoal keeps the sulphur from combining with the soda and potash. In sulphur ruby, a great part of the sulphur vaporizes in the working. The melting glass foams vigorously, and therefore one should fill the pot only half full at first, and after the batch reaches quiet fusion, put in the second half.

Sulphur ruby is hard to make in uniform colors, and darkens in the muffle. It is not used for making higher grades of glass. Two batches for sulphur ruby are given:

	No. 1	No. 2
Sand	100.0 kgm.	100.0 kgm.
Soda	45.0 kgm.	45.0 kgm.
$CaCO_3$	20.0 kgm.	20.0 kgm.
Flowers of sulphur	7.0 kgm.	10.0 kgm.
Antimony sulphate	5.0 kgm.	
Charcoal	2.0 kgm.	

EXPERIMENTAL DATA BY WRITER

The foregoing typical batches for ruby glass are but a few of a large number given in the literature pertaining to glass making. An examination of these shows a wide variation in composition, but all agree in that they are high in silica and contain tin. In copper ruby, the amounts of copper and tin vary widely in their ratios to each other. These copper rubies are probably used in the manufacture of flashed glass.

In the beginning of the following experimental work, samples of commercial copper ruby, both the quick-cooled colorless and ruby colored were obtained. The uncolored sample was broken into fragments, and different fragments were heated to different temperatures for various lengths of time. A small Hoskins electric furnace was used, and temperatures were read with a Leeds Northrup potentiometer, using a platinum, platinum-rhodium thermocouple.

The following results were obtained:

TABLES

PIECE NO.	MAXIMUM TEMPERATURE	TIME HELD AT MAX. TEMP.	REMARKS
	°C	*minutes*	
1	500	30	No change in color
2	500	60	No change in color
3	550	30	No change in color
4	550	60	No change in color
5	575	1	No change in color
6	575	30	No change in color
7	600	1	Very light amber
8	600	15	Very light amber
9	600	30	Bright amber, slightly darker than No. 8
10	600	60	Bright amber, same as No. 9
11	650	1	Bright amber, same as No. 9
12	650	30	Deep ruby, edges slightly softened
13	650	60	Same as No. 12, edges slightly softened
14	675	15	Same as No. 12, edges slightly softened
15	675	30	Same as No. 12, edges slightly softened
16	675	60	Darker than No. 15, edges slightly softened
17	700	1	Same as No. 10, edges slightly softened
18	700	30	Dark red, edges slightly softened
19	900	30	Grayish purple, opaque, softened out of shape

The rate of increase of temperature was a constant factor in all of these tests, as follows: ten minutes from room temperature to 300°C; 300°C to 500°C at rate of 50° per minute; 500°C to maximum temperature at a rate of 25° per minute.

The results seem to show that the color at any definite temperature is practically constant, and that the color change at that temperature is apparently instantaneous. However, time is

required for the temperature to even up through-out the thickness of the piece.

It will be noticed that the glass shows signs of softening at that temperature at which the strong color develops. This is probably the softening point Zsigmondy[14] refers to in the article previously quoted. It is observed that there is little or no apparent change in color brought out between 650° and 675°, giving a safe range for an annealing oven.

Most of the glass formulas observed were high in lead and in silica. Accordingly the following formula was selected, it being the upper silica limit for most glasses:

$$\left.\begin{array}{l} 0.5\ PbO \\ 0.5\ Na_2O \end{array}\right\} 3\ SiO_2$$

In order to determine a suitable method of working, several small batches of this glass were fused. The method adopted was as follows:

The glass was fused in Battersea crucibles in a small pot furnace using gas and compressed air. The temperature range required for firing and to make the glass liquid enough for pouring, was between 1480°C and 1520°C. One-half hour was taken for complete fusion of the lead glasses and one hour for the leadless glasses.

Not much trouble was experienced in reducing the copper oxide and preventing oxidation. Although a slight reducing flame was used, the presence of cream of tartar (about ½ per-cent) seemed to make reduction certain, if the time of heating was not too long.

When fusion was complete the glass was poured on a heavy cast iron plate 1 in. thick, and then rolled to a thickness varying from 2 to 5 m.m. The thinner portions usually cooled colorless, and the color developed in the thicker, slower cooled portions, i. e. turning red or opaque brown or black.

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[14] Ibid 4.

FORMULAS

MATERIAL	Series A, Glass No. 1	2	3	4	5	6	7	Series A_1, Glass No. 1	2	3	4
Na_2O	0.50	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500
PbO	0.50	0.500	0.500	0.500	0.500	0.500	0.500	0.300	0.300	0.300	0.300
CaO	....	.....	.....	.....	.....	.....	.....	0.200	0.200	0.200	0.200
SiO_2	3.00	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
CuO	0.04	0.004	0.004	0.002	0.001	0.0005	.....	0.004	0.003	0.002	0.002
SnO_2	0.04	0.004	0.010	0.007	0.007	0.007	0.007	0.010	0.010	0.010	0.007
Cream of tartar, percent	0.50	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500

BATCH WEIGHTS

	Series A							Series A_1			
Na_2CO_3	35.3	35.30	35.30	35.300	35.300	35.300	35.300	35.30	35.30	35.30	35.300
Pb_3O_4	57.0	57.00	57.00	57.000	57.000	57.000	57.000	.....	.....	.....	.....
White lead	....	.....	.....	.....	.....	.....	.....	34.30	34.30	34.30	34.300
$CaCO_3$	....	.....	.....	.....	.....	.....	.....	10.00	10.00	10.00	10.300
Flint	90.0	90.00	90.00	90.000	90.000	90.000	90.000	90.00	90.00	90.00	90.000
Cu_2O	1.4	0.14	0.14	0.070	0.035	0.018	0.000	0.14	0.10	0.07	0.070
SnO_2	3.0	0.30	0.75	0.052	0.052	0.052	0.052	0.75	0.75	0.75	0.052
Cream of tartar	1.0	1.00	1.00	1.000	1.000	1.000	1.000	1.00	1.00	1.00	1.000

SERIES A

Glass batches were then made corresponding to the formulas given in Series A.

The following results were obtained:

Number 1—Colored out very dense opaque grayish-brown color.

Number 2—(Decreasing the coloring agent.) This poured well, and cooled practically colorless at 5 m.m. thick. Softened out of shape at 675°C. and colored out, streaked with reddish color. At 700°C. it became dark brown, opaque and still streaked, very soft.

Number 3—(Increasing tin to harden.). This poured well and was colorless except for a pale greenish-yellow color at 5 m.m. thick.

Heated to 480°C, gives amber color,
Heated to 525°C, gives deep red color,
Heated to 700°C, softened out of shape giving a dense, brown opaque glass. Color change very rapid.

Number 4—(Decreasing the Cu_2O to reduce intensity of color). Color developed darker than No. 3 in pouring, having a greenish cast. Heated to 600°C, its color was deep opaque, and nearly black, amber at 550°C., and brown at 575°C.

Number 5—Developed a rather intense brown color while pouring. Thin colorless sections gave a deep greenish brown at 550°C. and a dense opaque black at 600°C.

Number 6—(Still reducing amount of coloring matter). This glass poured clear and colorless. On reheating, it changed to opaque black from 550°C. to 600°C. Color change very rapid.

Number 7—(Coloring matter left out to test purity of materials for iron). This glass on reheating at various temperatures gave no change in color.

The conclusions from this series of glasses, (excluding No. 1)[15] are:

(1) Low amounts of copper seemed to increase the density

[15] This glass was not melted well enough to judge results.

or opacity of the color, and decrease the signs of red, giving greenish browns.

(2) An increase in the tin in No. 3 stopped the streakiness shown in No. 2.

(3) Glass No. 3 was the best glass in series A, giving a colorless glass when poured and cooled quickly. Reheating showed shades of good red at various temperatures. However, the color change is so rapid, it would be difficult to control uniformity of color.

SERIES A1

Series A_1 was constructed in order to obtain harder glasses than those in series A, by replacing PbO with CaO so as to raise their temperatures of softening, and to determine how this affects the range of color change.

Glass No. 1 of this series showed a dark brandy color on pouring, coloring out quicker than No. 3 series A, which contained the same equivalents of Cu and Sn. This glass did not soften out of shape on reheating at 700°C., as did glass No. 3, series A, but gave a dense opaque color. If it could be handled, without coloring in pressing, this glass gives a good transparent red at 5 m.m. thick, upon reheating to the proper temperature.

Glasses Nos. 2 and 3 (reducing Cu_2O). Colored out quite dense, on pouring becoming nearly opaque. When reheated above 600°C. the glass turned a deep opaque purple.

Glass No. 4 (reducing SnO_2). This glass seemed to color out as rapidly as Nos. 2 and 3.

The conclusion which may be drawn from this series is that the rapidity of precipitation, or growth of color is increased, instead of decreased, as would be expected by hardening the glass.

SERIES B

The basal formula for this series is one of the published formulas given in Sprechsaal.[16] It is a high lead, low silica glass, containing some borax and is a much softer glass than series A and A1.

[16] Ibid 10.

FORMULAS

Series B

GLASS NO.	Na_2O	PbO	K_2O	SiO_2	CuO	SnO_2	MnO_2	Fe_2O_3	B_2O_3	CREAM OF TARTAR
										percent
1	0.101	0.623	0.202	2.31	0.0668	0.018	0.0079	0.0042	0.0725	0.5
2	0.102	0.627	0.202	2.33	0.0670	0.018	......	0.0042	0.0730	0.5
3	0.101	0.623	0.202	2.31	0.0668	0.018	0.0079	......	0.0725	0.5
4	0.102	0.627	0.202	2.33	0.0670	0.018	......	......	0.0730	0.5
5	0.102	0.627	0.202	2.33	0.0670	.....	......	......	0.0730	0.5
6	0.102	0.627	0.202	2.33	0.0670	.....	......	0.0042	0.0730	0.5
7	0.101	0.623	0.202	2.31	0.0668	.....	0.0079	0.0042	0.0730	0.5
8	0.119	0.627	0.202	2.33	0.0500	0.018	......	......	0.0730	0.5
9	0.129	0.627	0.202	2.33	0.0400	0.018	......	......	0.0730	0.5
10	0.139	0.627	0.202	2.33	0.0300	0.018	......	......	0.0730	0.5
11	0.098	0.627	0.202	2.33	0.0710	0.018	......	......	0.0730	0.5
12	0.092	0.627	0.202	2.33	0.0770	0.018	......	......	0.0730	0.5
13	0.102	0.627	0.202	2.33	0.0670	0.023	......	......	0.0730	0.5
14	0.102	0.627	0.202	2.33	0.0670	0.067	......	......	0.0730	0.5
15	0.102	0.627	0.202	2.33	0.0670	0.134	......	......	0.0730	0.5

The results showed this very markedly. The fusions, made at the same temperature range 1480°C and 1520°C, were more fluid and poured easier.

Numbers 1, 2, 3 and 4 developed deep opaque glasses when poured 4 to 5 m.m. thick. The thinner portions, however, increased in degree of transparency to about 2 m.m. at which thickness the glasses cooled colorless, but of course very brittle. Upon reheating, the colorless pieces of these four glasses colored to about the same color density when heated to the same temperature. At 500°C, they showed an amber color changing to a light red at 525°C., and to a ruby color at 550°C., becoming opaque at 600°C. Leaving out the iron, or manganese or both, (especially the latter), seemed to improve the quality of the red and to give a less dense color. This type of glass gives a much better red color than any of series A, but it is impossible to work with sections as thick as commercial glass pieces would be made and still obtain a transparent color. However, it would work as a ruby glass in making flashed articles and give a good color. Manganese dioxide and Fe_2O_3 are detrimental rather than helpful in obtaining good colors.

In series B, Numbers 5, 6 and 7 (in which SnO_2 is absent), the glasses were more opaque in all cases. Number 7 colors out even in the thin sections to a dense black.

In glasses Nos. 8, 9, 10, 11 and 12, the tin was kept constant and the copper varied. In all cases the tendency was to increase opacity and the rapidity in which the color appeared on pouring.

In glasses Nos. 13, 14 and 15, in which the tin was increased, no beneficial results were obtained, since these glasses were more opaque than the preceding ones in the group.

The ruby color in glasses as soft, and as low in SiO_2 as the members of this group cannot be controlled. However, when B1 and B2 were melted, quenched in water and remelted, there was an improvement, since all signs of streakiness disappeared, and the color became very uniform on reheating.

BATCH WEIGHT

Series B

GLASS NO.	FLINT	POTASH	WHITE LEAD	BORAX	SODA ASH	Cu_2O	SnO_2	Fe_2O_3	MnO_2	CREAM OF TARTAR
										percent
1	100	26.0	30	10	13.2	3.50	2.00	0.5	0.5	1.0
2	100	26.0	30	10	13.2	3.50	2.00	0.5	...	1.0
3	100	26.0	30	10	13.2	3.50	2.00	...	0.5	1.0
4	100	26.0	30	10	13.2	3.50	2.00	...	...	1.0
5	100	26.0	30	10	13.2	3.50	....	...	...	1.0
6	100	26.0	30	10	13.2	3.50	....	0.5	...	1.0
7	100	26.0	30	10	13.2	3.50	....	0.5	0.5	1.0
8	100	26.0	30	10	17.2	2.60	2.00	...	...	1.0
9	100	26.0	30	10	18.8	2.10	2.00	...	...	1.0
10	100	26.0	30	10	20.6	1.56	2.00	...	...	1.0
11	100	26.0	30	10	12.4	3.70	2.00	...	...	1.0
12	100	26.0	30	10	11.2	4.03	2.00	...	...	1.0
13	100	26.0	30	10	13.2	3.40	2.55	...	...	1.0
14	100	26.0	30	10	13.2	3.40	7.45	...	...	1.0
15	100	26.0	30	10	13.2	3.40	14.90	...	...	1.0

The basis of this series obtained from Hohlbaum[17] is entirely different than series B. It is a lime-potash, high silica, leadless glass, with high tin, therefore, a comparatively refractory and viscous glass at low temperatures. One hour was taken for fusion.

Hohlbaum's batch calls for SnO as the reducing agent, cream of tartar being added as a precaution to insure sufficient reduction. Number C-I was first made by substitution of SnO_2 for SnO, and leaving out the cream of tartar. An oxidized clear colorless glass was the result, giving no color change when reheated beyond the softening point.

Number C-I was again made using SnO_2 and 0.5 percent cream of tartar. This glass was exceedingly viscous and quickly cooled below the point of easy pouring. Upon pouring and rolling, (although taking a little more time), no color change took place, the glass remaining clear and colorless.

Upon reheating, no color change took place until

800°C. was reached, when a light amber color was obtained,

850°C. gave a pale reddish brown,

900°C. gave a light brown,

1000°C. softened with an opaque brown color.

The red color was not good in this glass and it seemed to be entirely too refractory.

Series C, No. 2. (Reducing SiO_2 to soften). This showed an improvement in the working qualities with no tendency to color out on pouring.

Reheating this glass gave the following results:

800°C. a distinct light red,

850°C. a good ruby color,

900°C. a deep dark red nearly opaque when 4 m.m. thick.

Series C, No. 3 (reducing SiO_2 still further) gave a fusion which poured colorless and flowed freely. Reheated to 850° it showed a reddish brown, slightly streaked. 900° showed a distinct deep brown.

[17] Ibid 11, p. 125.

FORMULAS
Series C

GLASS NO.	SiO_2	K_2O	CaO	CuO	SnO_2	PbO	Na_2O	B_2O_3	CREAM OF TARTAR
1	4.57	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
2	4.00	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
3	3.50	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
4	3.00	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
5	2.75	0.536	0.440	0.023	0.041	.....	.....	.....	0.5
6	4.57	0.536	0.240	0.023	0.041	0.200	.....	.....	0.5
7	4.00	0.536	0.240	0.023	0.041	0.200	.....	.....	0.5
8	4.00	0.536	0.340	0.023	0.041	0.100	.....	.....	0.5
9	4.00	0.536	0.340	0.023	0.041	.....	0.100	0.200	0.5
10	4.00	0.536	0.340	0.023	0.041	.....	0.100	.....	0.5
11	4.57	0.536	0.340	0.023	0.041	0.100	.....	.....	0.5
12	4.57	0.536	0.340	0.023	0.041	.....	0.100	.....	0.5

BATCH WEIGHTS

GLASS NO.	FLINT	POTASH	WHITING	Cu_2O	SnO_2	WHITE LEAD	SODA ASH	BORAX	CREAM OF TARTAR
1	200.0	68.0	32.0	1.2	4.46	....	....	....	2.0
2	175.0	68.0	32.0	1.2	4.46	....	....	....	2.0
3	153.0	68.0	32.0	1.2	4.46	....	....	....	2.0
4	131.0	68.0	32.0	1.2	4.46	....	....	....	2.0
5	120.0	68.0	32.0	1.2	4.46	....	....	....	2.0
6	200.0	68.0	17.4	1.2	4.46	29.4	....	....	2.0
7	175.0	68.0	17.4	1.2	4.46	29.4	....	....	2.0
8	175.0	68.0	25.0	1.2	4.46	15.0	....	....	2.0
9	175.0	68.0	25.0	1.2	4.46	....	....	22.9	2.0
10	175.0	68.0	25.0	1.2	4.46	....	10.4	....	2.0
11	200.0	68.0	25.0	1.2	4.46	15.0	....	....	2.0
12	200.0	68.0	25.0	1.2	4.46	....	10.4	....	2.0

Series C, No. 4 (less SiO_2 than C3). Poured clear and colorless but when reheated to 850° became more streaked and showed a more decided brown.

Series C, No. 5, poured clear and colorless as the others, but showed brown streaks. When reheated to 800° it showed a very streaked brown color. When the glass was remelted and repoured it gave a very clear glass.

Upon reheating this to 750°C. the color came out a clouded black, increasing in intensity with the reheating temperature.

The foregoing five glasses in group C show that:

(1) Reducing the SiO_2 from 4.57 to 4.0 molecules improved the color in this series. Further reduction, however, changed the color to browns and then blacks, giving about the same range of brown and blacks with 3 SiO_2 as series A gave, having 3 SiO_2 and small amounts of copper.

(2) High silica seems necessary in order to develop a good red color. The color change takes place at rather high temperatures for a reheating furnace, and the glass appears to be too viscous for good working properties. Glasses C6, C7 and C8 were made by introducing PbO in place of part of the CaO with the idea of softening and, if possible, still retaining the property of not coloring out on pouring.

C6 and C7 in which 0.2 PbO replaced 0.2 CaO showed a distinct improvement in the working qualities and uniformity of color, although these glasses colored out in the thicker portions during the pouring; C6 to a light red and C7 to a deep ruby. These glasses, however, were transparent to a thickness of 8 m.m. in comparison with series B, which were not transparent in pieces over 2½ m.m. in thickness.

Reheating clear portions of C6 gave a good, deep, ruby color at 650°C., a considerable lowering of the temperature over the leadless glasses for developing color. This glass also has a fairly constant color over a temperature range of 25°C (625° C. to 650°C).

Series C, No. 7 colored out at 570° to the same shade as C6.

Series C, No. 8 (Reducing PbO to 0.1 with 4.00 SiO_2). This glass gave evidences of being harder than the previous glass

(C7) as the fusion colored out a very little clearer at 6 m.m. thick (similar to C6), and the colorless portions gave a deep clear ruby on reheating to 570°, the same as C7 and about 60° lower than C6. This glass gave the clearest and best red obtained in the foregoing work.

Series C, No. 9 (in which 0.1 PbO was replaced in C8 by 0.1 Na_2O as borax) gave a glass considerably more fusible, and flowed well in pouring. A very streaked, nearly black, color developed in portions over 3 m.m. in thickness on pouring. Thin transparent pieces heated to 750° gave a red color, streaked with opaque black lines. This fusion, therefore, did not give good results. The possibility of spoiling the color by over-heating is ever present. It is possible that less B_2O_3 would give better results, though this was not tried.

Series C, No. 10 (0.1 Na_2O replacing 0.1 CaO). The resulting glass was clear and colorless, showing a very few light red streaks. The working properties of the glass were very good, especially in pouring and cooling.

On heating to 700°C the glass turned a clear light red.
625°C. showed a clear light red.
725°C. showed a clear light red.

The color range of this glass is therefore good.

Series C, No. 11 (0.1 PbO replacing 0.1 CaO and with 4.57 SiO_2). Results from this glass were a failure as the fusion was incomplete and very viscous and colored out a dense opaque black on pouring. If properly fused, better results would no doubt have been obtained.

Series C, No. 12 (0.1 Na_2O replacing 0.1 CaO and with 4.57 SiO_2). This glass gave a very good fusion, but was rather viscous and showed no color on pouring. Heating this glass to 700°C gave an amber colored glass streaked with dark red lines. At 800°C it showed a good even ruby color.

The conclusions from this last series of glasses (C6 to C12) are (1), that soda replacing lime softened the glass without causing the color to come out in cooling. (2) Lead on the other hand caused these glasses to color out rapidly on cooling, but did not make them opaque.

General Conclusions. The following are general conclusions one may draw from this work regarding the composition of a workable ruby glass. A workable ruby glass is one which will not color out when cooled at the rate obtained in the pressing process, and yet will give a workable range of temperature for reheating to a uniform color at temperatures below 700°.

1st. Highly fluid glasses will color out rapidly, viscous glasses slowly.

2nd. Replacing lime with either lead or soda, increases the rapidity of color development, lead more so than soda.

3d. High SiO_2 is necessary for good color, low SiO_2 gives a tendency towards brown or black, and opacity.

4th. High SiO_2 (4.0 to 4.5 mol.), is necessary to give sufficient viscosity.

5th. With high silica, lime-potash glasses the tendency to streakiness increases. Small amounts of lead reduce streakiness.

6th. The glass giving the best color in series B is No. 4. Glasses Nos. 1, 2, 10 and 12 of Series C, most nearly approached the requirements of a good ruby glass. They could all be poured without the color developing, and on reheating, the color developed at favorable temperatures. Glasses Nos. 6 and 8, Series C gave the most transparent colors.

7th. Iron and manganese are detrimental to a good red color.

8th. Remelting improves the uniformity of the color which indicates that streakiness is due to lack of homogeneity.

9th. Density of color is apparently increased with an increase in temperature. Time is evidently not an important factor in this case.

DISCUSSION

Prof. Silverman: There are a number of points in Mr. Williams' paper about which I wish to inquire. In the first place, he speaks of the coloring out in the high-silica copper rubies. I should like to ask whether Mr. Williams found any direct bearing by the alkali content of the glass. There is a claim

made at present that a copper ruby can be manufactured, which is a ruby, out of the pot. I believe his views correspond with mine in that the red color produced is due to high alkali in the glass. In other words, the glass colors out while cooling in the mold, or even earlier. Then as to tin as a reducing agent, I can corroborate these statements also, having had the experience that tin alone in connection with copper gives a rich color, while with manganese and iron the color is off. Tin has to be controlled very carefully. If you get below a certain point you obtain a glass which does not color sufficiently; and if you go above you get what is called clouding or a livery color.

I would like to ask, to what Mr. Williams attributes lack of uniformity of color; and whether he feels that a melt over a short duration, like thirty minutes could give a homogeneous glass.

Mr. Williams: To answer the last question first: the uniformity of color in my glasses was not obtained in the first melt. There were signs of streakiness at first, but upon remelting, good clear colors were obtained. It is probably the mechanical handling of the glass, or the duration of the melt which has a tendency to make the glass cloudy or clear.

The first question you asked, regarding the high alkali content, I did not quite understand, however I will make this point, that when I used lead, replacing the alkali, it caused the colors to come out more quickly in the handling. The color was just as good, in fact a little better, but density of color could not be controlled. Lead improved the uniformity of the color but gave a tendency toward opacity. If you do not want the color to come out during pressing, it is necessary to keep away from lead.

Prof. Silverman: I should like to know further, what the object is in trying to prevent the color from coming out during pressing.

Mr. Williams: If you do not prevent it, the different variations in the cooling of the mold would not give the same shading of red in the finished pieces.

Prof. Silverman: But do you not get the same effect by heating to a certain temperature afterwards?

Mr. Williams: Yes; but can you control the rate of cooling of glass in the mold sufficiently accurately as to give uniformity of color from piece to piece?

Prof. Silverman: I cannot quite see how that has a bearing on the rate of cooling. Suppose your glass does not color out below 700°. You might have a mold anywhere from 400° to 600°, and the fact that you have no color would be no indication that your mold temperature is correct. In other words, you have such a large range below the coloring-out temperature that it does not seem any better indication as to mold temperature, than if you had a glass that colored out, except possibly to tell you that the mold is too hot.

Mr. Williams: My experience with glass that colored out was that glass of various thicknesses was different in shade. The difference in temperature of a mold would influence the color. The coloring out at a definite temperature also depends upon the speed at which a glass cools through the small temperature range of color development. If the glass cools at a high rate of speed through this temperature, the colloidal copper would not come out in large enough particles to show color. If the cooling rate is slower the particles grow of sufficient size to give color.

Mr. Gelstharp: I should like to ask whether that was not sub-oxide of copper.

Mr. Williams: I used cuprous oxide.

Prof. Stull: Perhaps I might throw a little light on Prof. Silverman's question by stating, that among the things Mr. Williams is investigating is a study of the temperatures at which the copper ruby comes out, and the effect of length of time as well as temperature in bringing it out. That is why he is trying to secure colorless glass to begin with.